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Rapid solvent extraction of gold(III) with high molecular weight amine from malonate media

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ABSTRACT

A novel solvent extraction separation method has been proposed for the determination of microgram level concentration of gold(III) in real samples. It involves rapid and quantitative extraction of gold by *N*-*n*-decylaminopyridine, a high molecular weight amine (HMWA), in xylene from aqueous sodium malonate medium in the pH range 7 - 10. The gold(III) from an organic phase is stripped with 1 M HNO₃ acid and determined spectrophotometrically with stannouschloride. The effect of concentration of malonate, extractant, metal ion, pH of various diluents, stripping agents and other substances on the quantitative extraction of gold(III) have been assessed. The method is applicable for the separation and determination of gold(III) from binary mixtures, synthetic mixtures, alloys and pharmaceutical sample is discussed. The method is highly selective, simple and reproducible. The molar absorptivity and Sandell's sensitivity of Gold(III)-*N*-*n*-decylaminopyridine complex are ($6.5 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$) and ($0.0024 \text{ ug cm}^{-2}$), respectively which indicates the applicability of the method.

Keywords: solvent extraction, gold(III), xylene, synthetic mixtures.

INTRODUCTION

Gold is found in about 3.5 ppb in the earth's crust, often as 75 – 90% pure native gold that has been released by the weathering of sedimentary and igneous rocks [1]. The beauty and rarity of gold has led to its use in jewelry and as coinage metal, and as a standard for monetary systems throughout the world. Gold has also one of the most important noble metals due to its wide applications in industry and economic activity. In medieval times, gold was often seen as beneficial for health, an the belief that something that rare and beautiful could not be anything but healthy. Even some modern esotericists and forms of alternative medicine assign metallic gold with a healing power. Some gold salts do have anti-inflammatory properties and are used as pharmaceuticals in the treatment of arthritis and other similar conditions. However, only salts and radioisotopes of gold are of pharmacological value, as elemental (metallic) gold is inert to all the chemicals as it encounters inside the body [2]. Liquid-liquid extraction is one of the most efficient methods used to separate, concentrate and purify metal ions and organic compounds [3,4]. Solvent extraction has become an effective technique in the recovery and separation of gold [1,4,5]. Other extractants are reported for gold(III) are *N*-*n*-octylaniline [1], cynex 923 [6], tributylphosphate [7], phospholene [8], tri-*n*-octylamine [9], tri-*n*-butylphosphate [10], alamine [11]. The preconcentration of metals from complex matrices of natural samples obtained by using high molecular weight amine (HMWA) is well known [12] but little work has been reported on the extraction of gold, particularly by secondary amines. However, the solvent extraction technique using HMWA and ammonium salts is effective for extracting gold. It is also effective for the separation of gold from other associated elements. Some HMWA have been used for extraction, separation and determination of gold (III)

from real samples. Adogen-464 [4] in carbontetrachloride extracted gold(III) from 1.2 M HCl medium, Which required 5 min for equilibration. The extraction of gold with trioctylamine (TOA), trioctylmethyl ammoniumchloride [TOMA(Cl)] and trioctylmethyl ammoniumbromide [TOMA(Br)] [13] have been reported from hydrochloric or hydrochloric acid solution with atomic absorption spectrometry[1-5].

MATERIALS AND METHODS

Apparatus

A Shimadzu JascoV-503-UV-vis spectrophotometer with 1cm quartz cells was used for absorbance measurements and pH measurements were carried out with a Systronics Digital pH Meter Model No. 802.

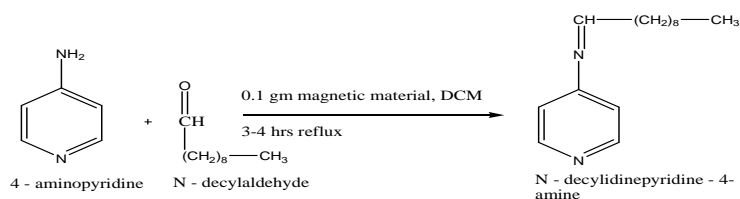
Reagents and chemicals

A stock solution of gold(III) was prepared by dissolving 1 g HAuCl_4 in dilute hydrochloric acid (1 M) and diluting to 100 ml with distilled water and further standardizing it [15]. A working solution $100 \mu\text{g ml}^{-1}$ was prepared from it by diluting the solution with triple distilled water. N-n-decylaminopyridine was prepared in xylene by the known literature method. A 10% solution of stannous chloride dehydrate in 1 M hydrochloric acid was used. A fresh solution was prepared weekly. The solutions of different metal ions used to study the effect of foreign ions were prepared by dissolving weighed quantities of respective salts in triple distilled water or dilute hydrochloric acid. Solutions of anions were prepared by dissolving the respective alkali metal salts in triple distilled water. All the chemicals used were of AR grade. triple distilled de-ionized water was invariably used throughout the measurements.

Synthesis of extractant

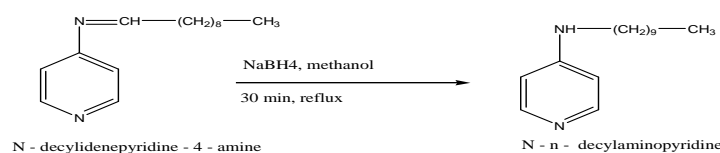
Step-1

N-n-decylaminopyridine was synthesized by equimolar proportion of N-decylaldehyde and 4-Aminopyridine in 20 ml DCM and 0.1 mg of metal catalyst and was refluxed for 3- 4 hrs. The product was separated and recrystallized from hot ethanol as white shiny needles (M.P- 68-70).



Step-2

Product of step1 (Schiff base) is reduced by NaBH_4 by taking equimolar amounts of Schiff base and NaBH_4 in absolute methanol and refluxed for 30 minutes, product was separated and recrystallized from hot ethanol (M.P - 245°C).



The purity of compound was monitored using ^1H NMR, FT-IR and Mass spectra. ^1H NMR (CDCl_3) : 0.87(3H,t- CH_3), 1.87(2H,d- CH_2), 1.26(2H,d- CH_2), 3.4(2H,s,- CH_2), 4.1 (1H,s,-NH),6.5 (2H,d,d, J 8 , Hz, aromatic protons), 8.2 (2H, d, J 8 Hz, aromatic protons). IR (cm^{-1}): 2922 (=C-H),1331(C-N),1513-1640 (C=C), 3429 (N-H). Mass m/e: 236 (100.0%) (M^+).

All chemicals used were of AR grade, doubly distilled water was used throughout.

Procedure

An aqueous solution containing $100 \mu\text{g}$ of gold(III)was mixed with a sufficient quantity of sodium malonate (0.2 g) to make its concentration, 0.025 M in a total volume of 25 mL of the solution. Then the pH range of the solution was

adjusted to 7-10, using dilute hydrochloric acid and sodium hydroxide. The solution was transferred into a 125 mL separating funnel and was shaken with 10 mL of (1×10^{-4}) M N-n-decylaminopyridine in xylene for 30 seconds. After equilibration, the mixture was allowed to separate and the metal ion was stripped from the organic phase with two 10 mL portions of 1 M HNO_3 acid. The extracts were evaporated to moist dryness and leached with dilute hydrochloric acid to form the solution. Gold(III) was estimated spectrophotometrically with stannous chloride at 400 nm

RESULTS AND DISCUSSION

Extraction as a Function of pH

Extraction of 100 μg gold(III) was carried out from 0.025 M sodium malonate at pH varying from 1 – 10. The extraction was found to be quantitative in pH range 7 - 10. This shows that the equilibrium in the pH range 7 -10 is favourable for the formation of an ion-pair complex. Hence pH 7 - 10 condition is maintain for further extraction studies.

Extraction as Function of Organic Acid Concentration

The extraction of gold(III) was carried out in pH range 7-10 with (1×10^{-4}) N-n-decylaminopyridine in xylene in the presence of varying concentration of sodium malonate and sodium succinate as weak acid media. The extraction commenced with 0.005 M sodium malonate and become quantitative in the concentration range 0.01 M – 0.05 M sodium malonate. With an increased concentration of sodium malonate there is a decrease in the efficiency of extraction of gold(III). Hence 0.025 M concentration of sodium malonate was therefore used through this work. Extraction was found to be incomplete in sodium succinate media.

Extraction as a Function of N-n-Decylaminopyridine

The gold(III) was extracted in pH range 7-10 with varying concentration of N-n-Decylaminopyridine at constant (0.025 M) sodium malonate concentration. The concentration of extractant was varied from 1×10^{-5} to 0.2 M in xylene. But extraction was quantitative in the range of 1×10^{-4} to 0.1 M of N-n-Decylaminopyridine. With increased concentration of extractant there was a decrease in the proportion of gold(III) extracted and this might be due to the dissociation of the complex. Hence 1×10^{-4} concentration was recommended for further studies.

Effect of diluents

Keeping all the variables constant the extraction of gold(III) were performed from malonate medium using 1×10^{-4} N-n-Decylaminopyridine with various diluents. The extraction was found to be quantitative with xylene, toluene, benzene, chloroform, carbon tetrachloride, dichloromethane. The extraction of gold(III) was found to be incompleting in methylisobutylketone(MIBK), isoamyl alcohol, n-butyl alcohol, isobutyl alcohol. An inert diluents such as xylene does not participate in the actual extraction process as do the oxygenated solvents. Xylene is recommended for further extraction procedure.

Nature of Extracted species

The composition of extracted species is ascertained by plotting graphs of $\log[\text{Au(III)}]$ against $\log C[\text{N-n-decylaminopyridine}]$ at fixed sodium malonate concentration (0.025). The plots were linear and having slope of 1.28 Also, plots of $\log D[\text{Au(III)}]$ against $\log C[\text{malonate}]$ at fixed N-n-Decylaminopyridine concentration 1×10^{-4} , were linear and having slope 2.09. The probable composition of the extracted species is calculated to be 1:2:1 (metal:acid:extractant).

Effect of time of equilibrium

Variation of the shaking period showed that a 15 s equilibration time was adequate for quantitative extraction of gold(III) from malonate media. But in our work, 1 min equilibration time was recommended in order to ensure the complete extraction of gold(III). However, a prolonged equilibration period more than 5 min was found to have an adverse effect on the extraction and should be avoided.

Loading capacity of N-n-decylaminopyridine

The concentration of gold(III) was varied to determine the loading capacity of 10 ml of 1×10^{-4} M N-n-decylaminopyridine was found to be 8.5 mg of gold(III).

Effect of Foreign Ions

Various ions were used in order to assess the tolerance of these ions on the extraction of gold(III). Gold(III) was extracted in the presence of different foreign ions (Table 1). The tolerance limit was set as the amount of foreign ions cause $\pm 2\%$ errors in the recovery of gold. The results showed that in the extraction and determination of 100 μg of gold, these ions did not interfere at the level tested. The reproducibility of gold extraction investigated from six replicate measurements was found to be $99.00 \pm 0.95\%$.

Table 1 Effect of Foreign Ions on the extraction of 100 μg Gold(III) at pH range 7 – 10 in 0.025 Malonate with 1×10^{-4} M N-n-decylaminopyridine in xylene.

Tolerance limit (mg)	Foreign ion added
100	Malonate, iodide, bromide, fluoride, acetate, nitrate
20	Mg(II), mn(II), ni(II), cu(II), co(II), fe(III)
15	Be(II), cr(III), pb(II), al(III), zn(II)
10	Hg(II), sn(II), sr(II), cd(II), Ti(IV)
5	U(IV), mo(VI), ce(IV), sb(III)
2	Ir(IV), ba(II), pt(IV) ^b , rh(III) ^a
1	Se(IV), Os(VIII), ru(III), pd(II) ^a
0	Ascorbate, EDTA

^a = masked with tartate ^b = masked with oxalate

Gold(III) = 100 μg ; aqueous phase = 0.025 M malonate; Aq/Org = 25:10; extractant = 1×10^{-4} M N-n-decylaminopyridine in xylene.

APPLICATIONS

Binary separation of gold(III) from base metals

The method allowed for separation and determination of gold(III) from binary mixture containing either iron(II), cobalt(II), nickel(II), copper(II). The separation of gold(III) from iron(II), cobalt(II), nickel(II), and copper(II) by its extraction with 1×10^{-4} M N-n-decylaminopyridine in xylene. Under these condition all the base metals remain quantitatively in the aqueous phase and these base metals were determined spectrophotometrically with thiocyanate [19], 1-nitroso-2-naphthol [19], DMG [19], and pyrimidine-2-thiol [20] respectively. Gold is stripped from the organic phase with two 10 mL portion of 1 M HNO_3 . The extract was evaporated to moist dryness and leached with 1 M hydrochloric acid to form the solution. Gold(III) was estimated spectrophotometrically with stannous chloride. Spectrophotometric methods are among the most precise instrumental methods of analysis for the determination of elements in trace amounts. An extractive spectrophotometric technique is a separation method [21]. These methods are remarkable for their versatility, sensitivity and precision. In these methods, a very extensive range of concentrations may be covered for the trace analysis of the elements [22]. The recovery of gold(III) and that of added ions was 99.7% and results are reported in Table 2

Table 2 separation and determination of Gold(III) from binary mixtures

Metal ion	Amount taken, μg	Average % Recovery*	Reference number
Au(III)	100 μg	99.8	16
Pd(II) ^a	100 μg	99.7	
Au(II)	100 μg	99.9	16
Pt(IV)	200 μg	99.7	
Au(III)	100 μg	99.9	16s
Rh(III) ^a	300 μg	99.8	
Au(III)	100 μg	99.8	16
Ru(III)	300 μg	99.8	
Au(III)	100 μg	99.9	17
Cu(II)	15000 μg	99.9	
Au(II)	100 μg	99.8	18
Co(II)	15000 μg	99.9	
Au(III)	100 μg	99.9	18
Ni(II)	10000 μg	99.9	
Au(III)	100 μg	99.8	18
Ni(II)	10000 μg	99.7	

* Average of six determinations ^a masked with tartarate

Separation of gold(III) from multicomponent synthetic mixture

A solution containing 100 µg of gold(III) was taken and known amounts of other metals added. Extraction of gold(III) was carried out using the method developed here. The results obtained were in good agreement with the amounts added (Table 3).

Table 3 Separation of gold(III) from multicomponent synthetic mixture

Composition, µg	Gold(III) found µg	Mean	Recovery %	RSD %
Au,100;Pt ^b ,500;Ru,200	199.7 199.7 199.8 199.7 199.8	199.74	99.92	0.07
Au,100;Pt ^b ,500;Rh ^a ,500	199.9 199.8 199.9 199.9 199.8	199.86	99.95	0.09
Au,100;Pt ^b ,200;Pd ^a ,500	199.8 199.8 199.8 199.9 199.9	199.84	99.94	0.06
Au,100;Pt ^b ,500;Ru,500;Pd ^a ,500	199.9 199.8 199.9 199.8 199.9	199.86	99.96	0.05
Au,100;Pt ^b ,500;Rh ^a ,500;Pd ^a ,500	199.8 199.7 199.8 199.8 199.7	199.76	99.98	0.07
Au,100;Fe,1000;Cu,1000;Ni,500	199.9 199.9 199.9 199.8 199.8	199.86	99.97	0.06

^a masked with tartarate^b masked with oxalate**Separation of Gold(III) in alloys**

To ascertain the selectivity of the reagent, the proposed method was successfully used in the determination of Gold(III) in alloys. The synthetic mixtures were prepared corresponding to the composition of alloy. The results of the analysis are reported in (Table 4). The average recovery of Gold(III) was 99.5 %.

Table 4 Analysis of Alloys

Composition of Alloy	Gold(III) found by AAS %	Gold(III) found by proposed method* %	Recovery %	RSD %
Cu,49.35;Ag,7.25;Au,43.4	44.3	43.1	99.7	0.18
Cu,35;Ag,5;Au,60	59.9	59.8	99.8	0.24

* Average of five determinations

Separation of Gold(III) from ayurvedic samples

The proposed method is applicable for the determination of gold content in the pharmaceutical samples. Dissolution of the sample is carried out by using the literature method [1]. An appropriate aliquot of the solution was taken for the analysis of gold content. The results of the analysis are reported in Table 5. The average recovery of gold(III) was 99.8 %. The accuracy of the results was confirmed using atomic absorption spectroscopy (AAS).

Table 5 Analysis of Gold(III) in Ayurvedic samples

Name of Medicine	Amount found by AAS, µg/mL	Amount found by proposed method* µg/mL	RSD %
Vita-Ex-Gold (Shree Baidyanath,Nagpur)	82	81.3	0.19
Suvarna Sootashekhar (Ayurveda Rasashala,Pune)	40	39.8	0.26
Makardhwaja Vati	36	35.9	0.24

* Average of five determination

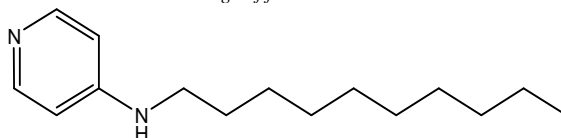


Fig.1. Structure of N-n-decylaminopyridine

CONCLUSION

In the present work, a simple, sensitive, inexpensive and selective method was developed for the extraction and separation of gold(III) from synthetic mixtures, alloys and Ayurvedic samples. The proposed method has several remarkable analytical characteristics:

- It is free from interference from the large number of diverse ions which are associated with gold(III) in its natural occurrence.
- The important features of this method are that low reagent concentration is required, and the time required for the equilibrium is very short (30 s).
- The method is effective to determine and separate gold from the alloys, synthetic mixtures and Ayurvedic samples.
- The method is very simple, selective and reproducible.

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